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A FURTHER INVESTIGATION
OF THE
CHLORIDES OF ORTHOSULPHOBENZOIC ACID.

Dissertation

Submitted to the Board of University Studies of
the Johns Hopkins University in conformity
with the requirements for the degree
of Doctor of Philosophy.

By

PHILIP HOWARD COBB.

1905.

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A FURTHER INVESTIGATION OF THE CHLORIDES OF ORTHOSULPHOBENZOIC ACID.

I. INTRODUCTION.

In 1889 Remsen and Dohme(1) allowed phosphorus pentachloride to react with the acid ammonium salt of orthosulphobenzoic acid. The chloride thus obtained was submitted to investigation. Its reactions with water, alcohols and ammonia were studied, and no evidence was obtained to cast doubt upon its chemical individuality. Remsen and Coates(2) studied the reaction of anilin upon the chloride, and obtained two isomeric products of the composition $C_{19}H_{16}N_2SO_3$. Thi led them to advance the hypothesis that the chloride thus prepared was in reality a mixture of two isomeric chlorides, one of the symmetrical, the other of the unsymmetrical structure. Remsen and Kohler(3) continued the work, and succeeded in isolating one of the constituents of the mixture in fairly pure condition. They found it to be a well crystallized substance melting at 76°. The other was

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(1) Am. Chem. J. 11, 332.
(2) Ibid. 17. 309.
(3) Ibid. 17. 309.

obtained as an oil which did not crystallize. Later Remsen and Saunders(1) obtained the same chloride in crystalline form. It melted at 21°.5 - 22°.5. Remsen and McKee(2) continued the work and were able to isolate the high-melting chloride in pure condition (melting point 79° - 79°.5). By crystallization of the mixed chlorides from ligroin they also obtained the chloride melting at 21°.5 - 22.5 . The melting point could not be changed by repeated crystallization. Though this substance was afterward shown to be composed of equal molecules of the high-melting chloride and another melting at 40 , the constituents seem to be held in loose chemical combination rather than in mechanical mixture. In the next year Remsen and Chambers(3) discovered that the chlorides could be separated by ammonia and the high-melting one obtained pure. In 1898 List and Stein(4) showed that the chloride melting at 21.5 - 22.5 was not pure, but that it consisted of a mixture of a chloride melting at 79.5 and another melting at 40°. They effected the separation by distilling the mixture under reduced pressure, and also originated the method which is now employed for the preparation of the low-melting chloride.

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(1) Loc. cit.
(2) Ibid. 18. 794.
(3) Ibid. 18. 791.
(4) Ber. d. chem. Ges. 31. 1648.

The action of the various reagents on the chlorides has been carefully studied(1) and the conclusion reached that to the high-melting chloride the symmetrical formula must be assigned, while the low-melting chloride has received the unsymmetrical formula. While the evidence forthe symmetrical nature of the former has been made clear, in the case of the latter more difficulty has been found in arriving at any definite conclusion. The products derived from the high-melting chloride are usually well characterized and their structures point definitely to the symmetrical nature of the chloride. Those derived from the low-melting chloride on the other hand, while sometimes characteristic, are often identical with those derived from its isomer, a fact which has made the problem a difficult one with which to deal.

II. PREPARATION OF MATERIALS.

The derivatives of orthosulphobenzoic acid employed in this investigation were prepared by methods which have been fully described by previous workers. No changes were introduced except in the preparation of the low-melting chloride, which will be described. Other reagents employed, sodium ethylate, phosphorus oxychloride and thionyl chloride, and the organic anhydrides were prepared by the usual methods.

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(1) Remsen, Am. Chem. J. 30. 247.

PREPARATION OF THE LOW-MELTING CHLORIDE.

The method formerly employed for the preparation of the low-melting chloride consisted in heating the neutral potassium salt with phosphorus oxychloride in a sealed tube for five hours or more. The temperature was not allowed to exceed 135°, since orthochlorbenzoyl chloride is formed at this point. The method here employed differs from the above only in that the mixture is heated in a flask and not under pressure. It was worked out by Mr. K. G. Falk.

One hundred grams of the dried and finely pulverized neutral potassium salt are placed in a 250 cc. round-bottom flask and 80 grams (1.5 mols.) phosphorus oxychloride are added. After thoroughly mixing the materials a cork bearing an air condenser is inserted in the neck of the flask, and the whole is heated in a bath of sulphuric acid or paraffine for fourteen hours at 130°. At the end of this time the mass is removed from the flask by a spatula and on cooling is ground with ice water in a mortar.

This treatment is necessary in order to remove the excess of the oxychloride and also the potassium chloride formed in the reaction. The washing is repeated several times. The undissolved portion which settles to the bottom of the mortar consists largely of the low-melting chloride. It is filtered off in a Buchner funnel provided with a muslin filter. After drying as thoroughly as possible on

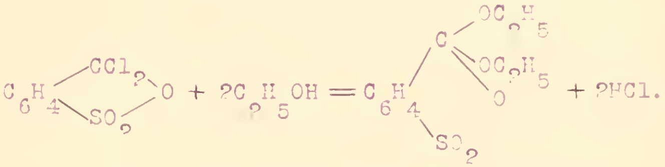
a porous plate the chloride is crystallized from ligroin. The melting point of the pure substance is 40°. A second crystallization may be necessary.

As it is impossible to dry the chloride thoroughly by means of a porous plate, and since the water remaining interferes considerably with the crystallization, it has been found advantageous to dissolve the chloride in ether at this point, and after filtering off any insoluble matter to dry the etherial solution over calcium chloride as in the case of the high-melting chloride. After filtration the ether is distilled off and the chloride crystallized as before.

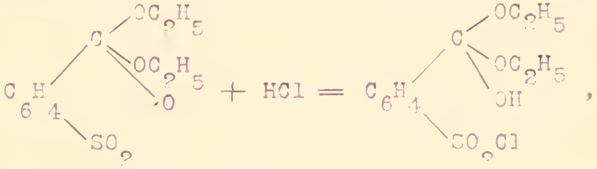
III. THE ACTION OF HYDROCHLORIC ACID ON ORGANIC ANHYDRIDES.

The action of alcohols on the low-melting chloride in the cold has been shown to consist in the formation of symmetrical esterchlorides, a fact which taken by itself would prove a strong argument for the symmetrical nature of the chloride. In the light of the other evidence however it is plain that this reaction is of no value in determining the structure of the chloride, and in view of the fact that all of the distinguishing reactions show it to be unsymmetrical, there must be some other explanation for the peculiar action of alcohol. It is always possible to assume a molecular rearrangement. A more tangible hypothesis would

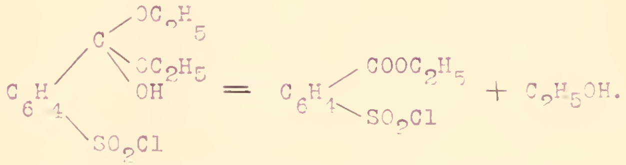
suggested by Remsen(1) however, in which he pointed out that the course of the reaction may be as follows: When ethyl alcohol is allowed to react upon the low-melting chloride, the first step in the reaction would be the substitution of the chlorine atoms by the ethoxy group, thus:



The anhydride would then take up hydrochloric acid,



and the product thus formed would lose alcohol and pass into the ester chloride without the assumption of any molecular rearrangement.



In order to test this view experimentally, the action of dry hydrochloric acid on various organic anhydrides was tried. On looking up the literature on the subject it was found that the reactions had been

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(1) Am. Chem. J. 30. 247.

recorded in the case of acetic(1), benzoic(2), benzoic acetic(3), and some others, while no mention of any experiments with the anhydrides of dibasic acids or inner anhydrides had been recorded. In order to become familiar with the conditions necessary to the success of the experiment, the work above referred to was repeated.

A quantity of acetic anhydride was placed in a small distilling bulb, a condenser was attached and the bulb heated on the water bath. Dry hydrochloric acid was led into the anhydride and reaction took place immediately. Acetyl chloride distilled into the receiver. After the distillation had ceased, the residue in the flask was examined and found to be acetic acid. The reaction is to be represented as follows:

$$\begin{matrix} CH_3CO \\ CH_3CO \end{matrix} \!\!> O + \begin{matrix} H \\ | \\ Cl \end{matrix} = \begin{matrix} CH_3COOH \\ + \\ CH_3COCl \end{matrix} .$$

The reaction of dry hydrochloric acid upon benzoic anhydride was found to be entirely analogous. The experiment was carried out both with the molten anhydride and with a benzene solution. Benzoic acid and benzoyl chloride were the products formed.

In the case of the mixed benzoic-acetic anhydride, the experiment was conducted as described above with acetic

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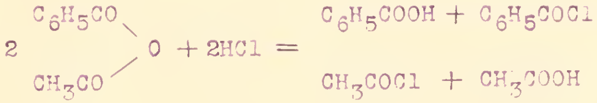
(1) H. Gal, Ann. Chim. Phys. (3) 66. 187.
(2) Kissling, Ann. Chem. 118. 303.
(3) Green, Bull. Soc. Chim. 33. 426.

anhydride. Four products, benzoic and acetic acids, benzoyl and acetyl chlorides, were obtained. No attempt was made to determine the relative amounts formed of each, since this had already been done as before stated. The reactions are



$$2\,\begin{matrix} C_6H_5CO \\ CH_3CO \end{matrix}\!\!>\!O + 2HCl = \begin{matrix} C_6H_5COOH + C_6H_5COCl \\ CH_3COCl + CH_3COOH \end{matrix}$$

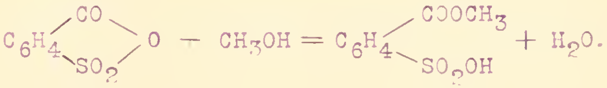
Having found that the anhydrides of monobasic acids react readily with dry hydrochloric acid, attention was turned to the inner anhydrides. Phthalic anhydride was first tried. A quantity of the anhydride was placed in a flask having a return condenser attached. By means of a tube passing through the cork and extending nearly to the bottom of the flask, the hydrochloric acid was admitted. Ether was used as the solvent. The ether was heated to boiling during the experiment. At the end of an hour the contents of the flask were examined but no reaction had taken place. Owing to the slight solubility of phthalic anhydride in ether, a greater part of it remained undissolved during the operation. Thinking that this fact might have hindered the reaction, a quantity of the anhydride was melted in a large test tube and kept molten for an hour while hydrochloric acid was passed through it. Considerable trouble was caused by the constant sublimation of the anhydride. It wasshown conclusively however that no change had taken place.

The conduct of succinic anhydride under these conditions was tried. Here the experiment was much more satisfactory than in the case of phthalic anhydride. Succinic anhydride is comparatively soluble in benzene. It also melts without sublimation. It was possible therefore to observe the effect of hydrochloric acid under the most favorable circumstances. A solution of the anhydride in benzene was heated to boiling on the water-bath for three hours, while hydrochloric acid was constantly passed through the solution. At the end of that time the benzene was distilled off and the anhydride was all recovered unchanged. In order to subject the anhydride to more energetic treatment, a quantity was placed in a test tube and was heated to its melting point (116°-117°) for an hour, in a bath of sulphuric acid. Hydrochloric acid was constantly passed through the molten material. At the end of that time the mass was cooled and examined. It was found to consist of unchanged succinic anhydride. Like treatment with hydriodic acid at a temperature of 150° failed to bring about a reaction after thirty minutes.

Finally sulphobenzoic anhydride was employed. It was thought probable that this substance would show a greater inclination to react than either of the dibasic anhydrides yet tried, on account of the presence of the sulphonic acid group. Such was not the case, however. The reaction was tried with the anhydride both in the molten state and in [illegible]

In order to observe the effect of hydrochloric acid under conditions as nearly as possible like those present in the reaction between alcohols and the low-melting chloride, the following experiment was performed.

Well cooled methyl alcohol in a test tube was saturated with dry hydrochloric acid, and to it was added five grams of sulphobenzoic anhydride. The tube was kept submerged in ice water and hydrochloric acid was passed through the solution. At this temperature the anhydride dissolved slowly and with no apparent evolution of heat. After one and one half hours the solution was poured into a beaker and the alcohol evaporated by drawing air through it, as has been described in preparing the orthosulphone chloride of methyl benzoate. The only product of this reaction was the orthosulphonic acid of methyl benzoate.

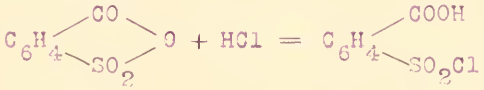


$$C_6H_4 \begin{cases} CO \\ SO_2 \end{cases} O + CH_3OH = C_6H_4 \begin{cases} COOCH_3 \\ SO_2OH \end{cases} + H_2O.$$

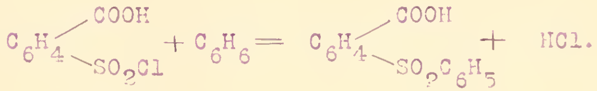
This experiment might be criticized on the ground that no evidence has been brought forward to show that the ester chloride is not first formed and immediately saponified to the acid. It has already been shown, however, that the orthosulphone chloride of methyl benzoate can be crystallized from alcohol, a fact which precludes an objection of this sort.

The final experiment was conducted with a view to determining whether the presence of a substance to react upon

the chloride is formed, could aid in bringing about a reaction between the anhydride and hydrochloric acid. Just as the presence of a reducing agent facilitates the attack of water by chlorine, so it was thought possible that the presence of benzene and aluminium chloride might aid in this case. Five grams of sulphobenzoic anhydride was dissolved in pure dry benzene contained in a small balloon flask. A return condenser was attached and the flask placed on the boiling water-bath. Hydrochloric acid was passed through the solution and aluminium chloride was added from time to time. After two hours the flask was taken down and its contents examined. No condensation product was obtained. Had the hydrochloric acid succeeded in breaking the anhydride ring the chloride thus formed should have condensed with the benzene to form phenylsulphon-orthocarbonic acid, thus:

I.


$$C_6H_4\begin{cases}CO\\SO_2\end{cases}O + HCl = C_6H_4\begin{cases}COOH\\SO_2Cl\end{cases}$$

II.


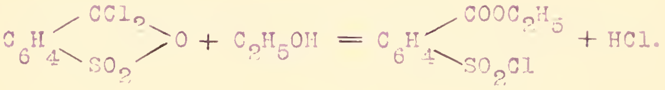
$$C_6H_4\begin{cases}COOH\\SO_2Cl\end{cases} + C_6H_6 = C_6H_4\begin{cases}COOH\\SO_2C_6H_5\end{cases} + HCl.$$

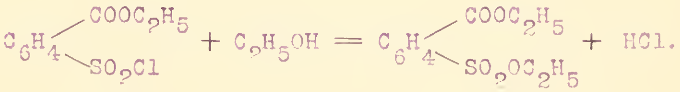
From these experiments it is seen that the anhydrides of the dibasic acids studied do not react with dry hydrochloric acid, while those of monobasic acids are easily attacked. Therefore the formation of symmetrical ester chlorides from the action of alcohol on the low-melting chloride does not seem to be dependent upon the

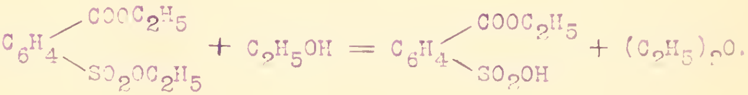
presence of hydrochloric acid. The formation of symmetrical esters from the action of sodium ethylate upon the low-melting chloride also seems to argue against this explanation.

IV. THE ACTION OF ALCOHOLS AND ALCOHOLATES ON THE CHLORIDES.

The action of alcohols upon the chlorides has been previously studied in this laboratory(1) as well as elsewhere(2) and has shown that the first products formed are ester chlorides which upon further action of the alcohol are transformed into the ester acids.

I.

$$C_6H_4\begin{cases}CCl_2\\SO_2\end{cases}\!\!>O + C_2H_5OH = C_6H_4\begin{cases}COOC_2H_5\\SO_2Cl\end{cases} + HCl.$$

II.

$$C_6H_4\begin{cases}COOC_2H_5\\SO_2Cl\end{cases} + C_2H_5OH = C_6H_4\begin{cases}COOC_2H_5\\SO_2OC_2H_5\end{cases} + HCl.$$

III.

$$C_6H_4\begin{cases}COOC_2H_5\\SO_2OC_2H_5\end{cases} + C_2H_5OH = C_6H_4\begin{cases}COOC_2H_5\\SO_2OH\end{cases} + (C_2H_5)_2O.$$

With the low-melting chloride the ester chloride is easily formed while its isomer is only slowly attacked by cold alcohol.

The work along this line was continued by R.M.Bird(3) who studied the action of the alcoholates as well. A brief

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(1) Remsen and Dohme; Karlslake, Am. Chem. J. 11. 341.
(2) List and Stein, Ber. d. chem. Ges. 31. 1659.
(3) Am. Chem. J. 30. 247.

summary of his results is as follows. The low-melting chloride when dissolved in cold methyl alcohol passed into the orthosulphone chloride of methyl benzoate. Upon evaporating the solution the substance separated in small diamond shaped crystals which melted at 57° - 58° (corr.). They were soluble in alcohol and ether, but insoluble in water. Cold dilute caustic soda did not affect the substance, but upon boiling it dissolved and chlorine was removed.

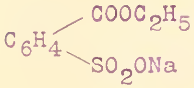
When the low-melting chloride was dissolved in methyl alcohol and the alcohol immediately boiled off, the orthosulphonic acid of methyl benzoate was obtained. Another product of this reaction was an oil which was shown to contain chlorine, and to it was assigned the formula of the above described orthosulphone chloride of methyl benzoate. It is not stated that the oil became crystalline, however.

The orthosulphone chloride of ethyl benzoate was obtained by treating dry low-melting chloride with an alcoholic solution of sodium ethylate until no more sodium chloride was precipitated. Upon extraction with ether and evaporation of the solvents, an oil remained insoluble in water, but soluble in alcohol and ether. When boiled with water it was hydrolyzed to an acid and hydrochloric acid was liberated. Treatment with ammonia yielded the orthosulphone amide of ethyl benzoate.

What was apparently the same oil was obtained by treating an alcoholic solution of sodium ethylate with an

etherial solution of the low-melting chloride. As a by-product of this reaction another oil was obtained which answered the description of the diethyl ester of ortho-sulphobenzoic acid obtained by Remsen and Dohme(1). It was soluble in water, alcohol, and ether, and contained no chlorine.

By this same treatment and two hours' standing before examining the products, the sodium salt of the formula



$C_6H_4\begin{cases}COOC_2H_5\\SO_2ONa\end{cases}$ was formed.

A slightly warm emulsion of 1.070 grams of sodium ethylate in absolute alcohol was gradually added to 1.996 grams of the low-melting chloride in etherial solution. The reaction progressed until one half of the ethylate had been added, when it suddenly stopped and could be induced to go no further. The resulting product was an oil. With dry ammonia, crystals were produced which melted at 225°-226°. They were acid toward litmus and potassium carbonate. The crystals yielded a sweet taste when boiled with strong ammonia, as did the oil when boiled with concentrated ammonia. Upon boiling the oil with water it was hydrolyzed to an acid. No formula was assigned to the substance.

An excess of ethyl alcohol was added to the low-melting chloride and boiled for thirty-five minutes. There

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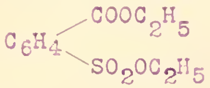
(1) Am. Chem. J. 11. 332.

resulted nothing but a neutral oil which was soluble in water, alcohol and ether; it contained no chlorine. Upon boiling with sodium hydroxide, ethyl alcohol was formed. The formula assigned was that of the diethyl ester:



$$C_6H_4\begin{cases}COOC_2H_5\\SO_2OC_2H_5\end{cases}$$

None of the compounds above described, with the exception of the orthosulphone chloride of methyl benzoate and the sodium salt of ethyl orthosulphobenzoate were analyzed. Certain considerations made it seem well to repeat the work:

1. The formation of ester chlorides by the action of sodium ethylate on the chlorides, and the impossibility of causing the reaction to go further.

2. The solubility of the so-called diethyl esters in water.

3. The production of a substance of acid reaction by boiling with ammonia.

4. The impossibility of obtaining the ester of a sulphonic acid by boiling its chloride with alcohol. Sulphonic acid esters are saponified by this process.

ACTION OF METHYL ALCOHOL ON THE LOW MELTING CHLORIDE.

Ten grams of the low-melting chloride were dissolved in thirty or forty cc. of cold methyl alcohol, and the solution allowed to stand two hours. At the end of that

time the alcohol was evaporated by warming the solution and drawing air through it. When the proper concentration had been reached, very small diamond shaped crystals separated from the solution. The evaporation was continued until no more crystals separated, when they were filtered off and washed with water to remove the alcohol and hydrochloric acid which is formed in the reaction. The substance agreed in all its chemical properties with that prepared by Bird. It is soluble in alcohol and ether, but insoluble in water. Cold alkali, whether concentrated or dilute, has no effect upon the substance, but on boiling it dissolves and chlorine is removed. The melting point, 63° - 64° (uncorr.) is somewhat higher than that given by Bird, but it is probable that his material was somewhat impure, since his analytic figures differ considerably from the calculated values.

Upon analysis the substance yielded the following figures(1).

I. 0.1062 gram gave 0.1592 gram CO_2 and 0.0276 gram H_2O.

II. 0.2354 gram gave 0.2401 gram $BaSO_4$ (Carius).

To determine the chlorine the substance was saponified by heating with pure caustic soda and then titrated

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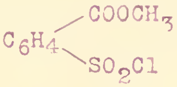
(1) The method employed for the determination of carbon and hydrogen was devised by Professor H.N.Morse. Mr.L.S. Taylor of this laboratory has made the development of this method the subject of his dissertation. See Morse and Taylor, Am.Chem.J.33. . See also L.S.Taylor, Dissertation, J.H.U. 1905.

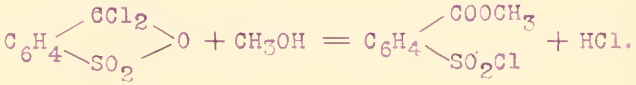
to neutrality with nitric acid. The chlorine was then determined with atenth normal solution of silver nitrate. Sodium chromate was used as the indicator.

III. 0.1835 gram required 7.8cc. $\frac{N}{10}$ $AgNO_3$.



Calculated for $C_6H_4\begin{matrix} COOCH_3 \\ SO_2Cl \end{matrix}$		Found.
C	40.90%	40.88%
H	3.01	2.92
Cl	15.11	15.06
S	13.66	14.00

The reaction is to be expressed as follows:



$$C_6H_4\begin{matrix} CCl_2 \\ SO_2 \end{matrix}\!>\!O + CH_3OH = C_6H_4\begin{matrix} COOCH_3 \\ SO_2Cl \end{matrix} + HCl.$$

The action of boiling ethyl and methyl alcohols has been fully investigated by former workers(1). The reaction with methyl alcohol was repeated and the product was found to be ester acid. No trace of the oil containing chlorine as described by Bird was obtained. The analogous reactions with ethyl alcohol have already been given on page 12.

ON THE HIGH MELTING CHLORIDE.

On the high melting chloride the alcohols in general react with less ease than upon the low melting chloride.

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(1) Remsen and Dohme, Am. Chem. J. 11. 341.
Remsen and Karslake, Am. Chem. J. 18. 325

Upon boiling, however, the ester acids are also produced.

By boiling either chloride with 95% ethyl alcohol for some hours, Bird obtained an acid of which the barium salt contained from 28% to 29.5% of barium. Humphreys(1) had already obtained the same acid by boiling the ortho-sulphone chloride of phenyl benzoate for twelve hours in absolute alcohol.

In the course of this investigation the reaction described by Bird was repeated with the hope of obtaining some light on the composition of this acid. Five grams of the high-melting chloride were boiled for thirteen hours with absolute ethyl alcohol. The formation of ethyl chloride was continuous. After the reaction was over the alcohol was distilled off and the remaining hydrochloric acid was expelled by heating on the water-bath. The material remaining was dissolved in water, filtered from the small insoluble residue and boiled with barium carbonate until no more was dissolved. After crystallization was dried and analyzed for barium. .1800 gram gave .0868 gram $BaSO_4$. Found: Ba 28.37%. This was evidently the same acid which had been obtained by Humphreys and Bird. Since no formula could be assigned to the substance form the analysis of its barium salt, an effort was made to get at its structure in another way. The experiment was repeated

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(1) See Dissertation, J.H.U. 1900

with an equal quantity of the chloride and the barium salt prepared as before. This was converted into the sodium salt and after evaporating to dryness, the salt was ground in a mortar with phosphorus pentachloride. Reaction took place immediately. After heating some time to expel the oxychloride, water and ice were added and the material was ground until all traces of the oxychloride had been removed. After washing several times with water, strong ammonia was added and the mixture was warmed on the water-bath. The solutions became sweet and when hydrochloric acid was added a heavy precipitate of saccharine appeared. This experiment pointed to the presence of orthosulphobenzoic acid. The following considerations lead to the same conclusion. The action of boiling alcohol on the chlorides is known to produce the ester acid. Further action of the alcohol produced the unidentified acid. The action of alcohol on the phenyl ester chloride must first convert it into the ester acid. Upon further boiling the same unidentified acid was also formed. These facts show that a change in the carboxyl group must have taken place. The action of phosphorus pentachloride already referred to showed the acid to be dibasic. The ethyl esters of of carboxyl acids are not saponified by absolute alcohol, however, and a special reason must be sought in this case. It has been stated that ethyl chloride formed constantly and for every molecule of ethyl chloride, one molecule of water must have resulted. The tendency

of the water should be to saponify the ester and there would result an equilibrium between orthosulphobenzoic acid and the ester acid. In the experiments performed by Bird he obtained the acid after three hours' boiling with 95% alcohol, while in the experiments last described thirteen hours' heating with absolute alcohol was required. Providing that all of the hydrochloric acid formed in this reaction reacted with the alcohol, then for every molecule of chloride used enough water would be formed to saponify two molecules of the ester acid. The presence of the alcohol would cause an equilibrium to exist between the ester acid and orthosulphobenzoic acid. It appears therefore that the salt containing about 28 per cent barium is probably a mixture of a salt of orthosulphobenzoic acid and a salt of the ester acid.

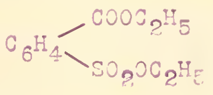
V. ACTION OF SODIUM ETHYLATE.

HIGH MELTING CHLORIDE.

Five grams of the high melting chloride were dissolved in dry ether and an alcoholic solution of sodium ethylate was gradually added until the reaction ceased. The reaction is best carried on in a bottle so that it may be corked and well shaken from time to time, since the precipitated sodium chloride is voluminous and interferes with the reaction. In no case were less than two molecules of ethylate required. The reaction never stopped half-way, and an addition of an excess of ethylate [illegible] found necessary to

order that the reaction might be complete. After the reaction was over, the resulting mixture was poured into a separating funnel containing acidulated water. The contents was thoroughly shaken until the sodium chloride and excess of ethylate were dissolved, when the aqueous layer was run off. The ethereal layer was washed several times with water, then removed and dried over calcium chloride for twelve hours. After filtration and evaporation of the ether an oil remained which was soluble in alcohol and ether but insoluble in water. It was neutral to litmus. Various methods for its purification were tried, but none were successful until distillation under reduced pressure was attempted. A portion of the substance thus purified gave the following figures on analysis.

I. 0.1540 gram gave 0.2899 gram CO_2 and 0.0738 gram H_2O.
II. 0.3493 gram gave 0.3243 gram $BaSO_4$.

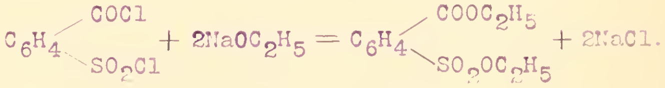


Calculated for $C_6H_4\begin{matrix}COOC_2H_5\\SO_2OC_2H_5\end{matrix}$		Found.
C	51112	51.33
H	5.47	5.37
S	12.41	12.74

These figures point conclusively to the formula of the diethyl ester. It boils at 212° - 213° under 21mm. pressure. At this pressure the ester distills with very little decomposition. It should be allowed to stand after distillation, however, for some hours as [illegible] crystals of

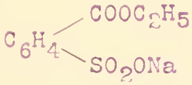
sulphobenzoic anhydride usually separate. They can be removed by filtration. At a greater pressure, however, the ester distills with much decomposition. Among the products formed are sulphobenzoic anhydride and ethyl benzoate. The former was identified by its melting point (129°.5), and by its conversion into sulphone fluorescein when fused with resorcinol. The latter was detected by its odor.

Reaction:



$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases} + 2NaOC_2H_5 = C_6H_4\begin{cases}COOC_2H_5\\SO_2OC_2H_5\end{cases} + 2NaCl.$$

The yield of ester by this method was always small. The fact determined by Bird that when the reaction is allowed to stand a salt of the formula



$$C_6H_4\begin{cases}COOC_2H_5\\SO_2ONa\end{cases}$$

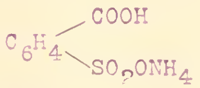
is formed suggested the explanation of the small yield. The alcohol used as the solvent for the ethylate would tend to saponify the ester, and the acid thus formed would be converted into its sodium salt by the action of the ethylate. To test this point the experiment was repeated as above with the exception that no alcohol was used, the ethylate being added in the dry state to the ethereal solution of the chloride. The yield of ester was almost theoretical. No sulphone chloride was obtained in the experiments.

Upon boiling the impure ester with ammonia [illegible] [illegible] was usually produced, [illegible] [illegible] precipitate

of saccharin appeared upon acidification. No such reaction takes place with the pure ester, however. Furthermore the impure ester always gives a test for chlorine, while the pure substance is entirely free from it. These facts show that a small quantity of unchanged chloride is usually present in the impure ester. They also tend to explain certain observations made by Bird, which have already been referred to.

It is a fact that the action of ammonia upon the ester produces a substance which has an acid reaction. The ester is boiled with frequent additions of concentrated ammonia until it dissolves. This operation requires half an hour or longer. The solution is then evaporated to the proper concentration and allowed to cool. If the ammonia gas has all been expelled from the solution, the acid ammonium salt of orthobenzoic acid separates. A determination of the nitrogen in the salt showed this to be the case.

0.1097 gram gave 0.006858 gram nitrogen (absolute).

Calculated for 

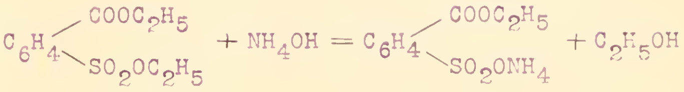
$C_6H_4\begin{cases}COOH\\SO_2ONH_4\end{cases}$

Found.

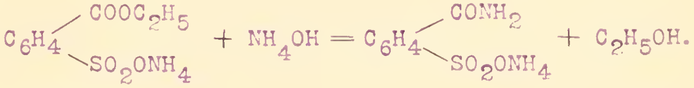
N_2 6.40% 6.25%

In order to obtain confirmatory evidence if possible, a quantity of the acid ammonium salt of orthosulphobenzoic acid which had been made by the hydrolysis of saccharine was dissolved in an excess of strong ammonia, and the solution evaporated. After the odor of ammonia had disappeared the solution was found to have become acid

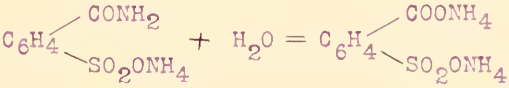
and crystals of the acid ammonium salt were obtained upon further evaporation. Ammonium benzoate was found to behave in the same way. The reactions must be expressed as follows:

I. 

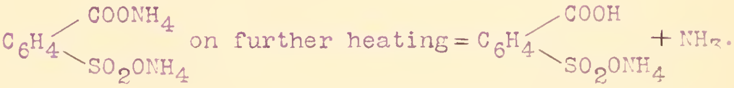
$$C_6H_4\begin{matrix}\diagup COOC_2H_5\\ \diagdown SO_2OC_2H_5\end{matrix} + NH_4OH = C_6H_4\begin{matrix}\diagup COOC_2H_5\\ \diagdown SO_2ONH_4\end{matrix} + C_2H_5OH$$

II. 

$$C_6H_4\begin{matrix}\diagup COOC_2H_5\\ \diagdown SO_2ONH_4\end{matrix} + NH_4OH = C_6H_4\begin{matrix}\diagup CONH_2\\ \diagdown SO_2ONH_4\end{matrix} + C_2H_5OH.$$

III. 

$$C_6H_4\begin{matrix}\diagup CONH_2\\ \diagdown SO_2ONH_4\end{matrix} + H_2O = C_6H_4\begin{matrix}\diagup COONH_4\\ \diagdown SO_2ONH_4\end{matrix}$$

IV. 

$$C_6H_4\begin{matrix}\diagup COONH_4\\ \diagdown SO_2ONH_4\end{matrix} \text{ on further heating} = C_6H_4\begin{matrix}\diagup COOH\\ \diagdown SO_2ONH_4\end{matrix} + NH_3.$$

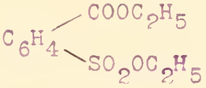
With saponifying agents, the first point of attack is the sulphonic acid group. With aqueous alkali the ester is only slowly attacked owing to its insolubility in water, but when alcoholic alkali is employed the reaction proceeds with ease. The final product of the action of alkalis is the neutral salt of orthosulphobenzoic acid. Aqueous ammonia acts more easily than aqueous alkali.

LOW MELTING CHLORIDE.

The action of sodium ethylate on the low melting chloride also results in the formation of the diethyl ester. The ester agrees in all its properties with the one prepared from the high melting chloride. On analysis the foll

owing figures were obtained.

0.1537 gram gave 0.2863 gram CO_2 and 0.0794 gram H_2O.



	Calculated for $C_6H_4(COOC_2H_5)(SO_2OC_2H_5)$	Found
C	51.12%	51.46%
H	5.47	5.86

The reaction was tried under various conditions, an alcoholic solution of sodium ethylate was added to dry chloride: the chloride in ether was treated with analcoholic solutions of the ethylate, and fimally dry ethylate was added to an ethereal solution of the chloride. The last was found to be the most satisfactory method.

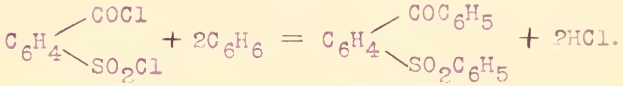
The neutral oils soluble in water which are described by Bird have not been obtained. Their solubility precludes the possibility of their being esters however.

An unidentified product was obtained by Bird on grinding together dry sodium ethylate and dry low-melting chloride. The reaction is explosive, and difficult to control. Furthermore, more or less decomposition takes place. In repeating the reaction the substances were mixed in very small portions in a large test tube and were stirred with a glass rod. After the reaction water and ether were added and the tube was shaken. The ether was found to contain a little oil in a very impure state and was not enough for distillation. It was neutral and insoluble in water, however, and there seems to be no rea

for doubting that it was the diethyl ester.

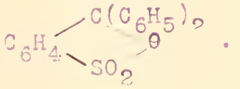
VI. ACTION OF BENZENE AND ALUMINIUM CHLORIDE.

The action of benzene in the presence of aluminium chloride on the chlorides was first studied by Remsen and Saunders(1). They showed that the high-melting reacts to form, as the final product, orthobenzoyldiphenylsulphone as follows:



$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases} + 2C_6H_6 = C_6H_4\begin{cases}COC_6H_5\\SO_2C_6H_5\end{cases} + 2HCl.$$

This substance melts at 183° - 184°. In studying the reaction with a mixture of the two chlorides, by far the larger portion of the product was the same substance. They obtained at the same time, however, another substance melting at 162 - 163. Analysis showed it to be of the same empirical formula as the above compound, but its conduct when fused with potash led them to assign to it the formula of the lactone,



$$C_6H_4\begin{cases}C(C_6H_5)_2\\ \qquad\quad O\\SO_2\end{cases}.$$

In their article upon the chlorides of orthosulpho-benzoic acid List and Stein(2) also describe the substance. They obtained it by the action of benzene and aluminium chloride upon the mixed chlorides. The reaction was allowed to proceed at ordinary temperatures for some days, after

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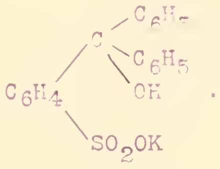
(1) Am. Chem. J. 17. 347.
(2) Ber. d. chem. Ges. 31. 1648.

which the mixture was warmed for a time. The substance dissolved in boiling alcoholic potash with the formation of a potassium salt with the formula



Upon treatment with acids the lactone was recovered.

Since it has been possible to isolate the low-melting chloride in pure condition many attempts have been made to prepare this substance. None of them has been successful, the sole product of the reaction being always the symmetrical compound orthobenzoyldiphenylsulphone identical with that derived from the high-melting chloride.

The writer made several attempts to obtain the lactone by the action of benzene and aluminium chloride upon the low-melting chloride, but always without success. The reaction was allowed to take place at the room temperature, during a period of three or four days, and also at the temperature of the water bath, when it is complete in a short time. Finally a mixture of 60 per cent of the low-melting chloride and 40 per cent of the high-melting chloride was dissolved in pure dry benzene, and aluminium chloride was added from time to time. The reaction was allowed to proceed at the room temperature. The resulting

product was found to be symmetrical, however, no trace of the lactone being formed. The proportion of the two chlorides taken is about that in which they occur in the mixture which is obtained by the action of phosphorus pentachloride on the acid potassium salt. It was with this mixture that List and Stein obtained their results.

From the experiments of former workers as well as from those last recorded, it would seem doubtful if the product first described by Remsen and Saunders, and later by List and Stein, was in reality the lactone as supposed. A substance has been obtained, however, and will be described presently, which analysis shows to be the lactone, and which, moreover, agrees with the description of the lactone made as above. Such being the case, the conclusion must be that the action of benzene and aluminium chloride has in two instances at least given the lactone. From the failure of other workers to obtain it, it is evident that peculiar conditions must be necessary to its formation.

VII. EXPERIMENTS WITH THIONYL CHLORIDE.

Since the methods which are employed for the preparation of the chlorides, especially in the case of the low-melting chloride, fail to give satisfactory yields, it seemed desirable to try the action of thionyl chloride on both the acid and neutral salts, in the hope that this reagent might prove preferable to either the pentachloride or oxychloride of phosphorus.

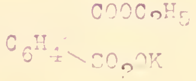
Ten grams of the dried and finely pulverized neutral potassium salt of orthosulphobenzoic acid was placed in a small balloon flask and an equal weight (2.5 mol.) of thionyl chloride was added. The flask was fitted to a return condenser which was provided at its upper end with a Peligot tube containing a strong solution of caustic soda to absorb the sulphur dioxide which was given off. The reaction started without the application of heat but did not become vigorous. At the temperature of the boiling water bath, however, it progressed rapidly. The heating was continued until no more sulphur dioxide was liberated, about forty-five minutes being required. During the progress of the reaction the mass became more and more viscous, until at the end the appearance had become like that of thick starch paste. The condenser was then reversed and the excess of thionyl chloride was distilled off. This process was much facilitated by slightly diminishing the pressure. After the removal of the excess of thionyl chloride, the mass became crystalline. It was removed from the flask and ground in a mortar with water containing ice, and then poured into a separating funnel and shaken with ice water and ether. A portion of the material did not immediately go into solution but dissolved gradually as the shaking was continued. After removing the ethereal layer it was [illegible]ized with the expectation of finding one or both of the chlorides of orthosulphobenzoic acid. All that was, how-

obtained, however, was a small quantity of the anhydride of orthosulphobenzoic acid which had escaped hydrolysis in the treatment with water. A portion of this material which did not dissolve readily was filtered off and examined. It was found to contain potassium and chlorine, and to show an acid reaction with litmus. On boiling with water it was dissolved and hydrochloric acid was formed. A small quantity was dried on a porous plate and placed in a desiccator over sulphuric acid. It was hoped in this way to obtain a specimen for analysis in fairly pure condition, but upon opening the desiccator some hours later, fumes of hydrochloric acid escaped showing that the substance had become hydrolyzed. No further effort was made to obtain the pure substance, but evidence for its composition was obtained by another method.

The reaction between the neutral salt and thionyl chloride was repeated in the manner above described, but after distilling off the excess of the latter, absolute alcohol was added and the mixture boiled. At the end of an hour the alcohol was filtered off. Upon cooling crystals separated in the form of thin leaves: these were filtered off and analyzed for potassium:

0.1050 gram gave 0.334 gram K_2SO_4.

Calculated for

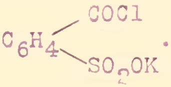


$C_6H_4 \begin{matrix} \diagup COOC_2H_5 \\ \diagdown SO_2OK \end{matrix}$

Found.

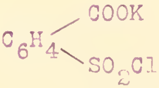
K 14.59% 14.22%

The yield of these crystals was only about 0.5 gram showing that the reaction had for the most part progressed beyond the first stage. That even a small quantity of this salt was obtained, however, points conclusively to the presence of a compound of the formula



$$C_6H_4\begin{cases}COCl \\ SO_2OK\end{cases}.$$

That the structure of this monochlorinated derivative of the neutral potassium salt is that which has been assigned to it, rather than that of the isomeric sulphone chloride

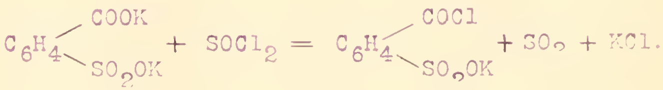


$$C_6H_4\begin{cases}COOK \\ SO_2Cl\end{cases}$$

is evident from the fact that it is esterified upon boiling with alcohol, a reaction which does not take place with the sulphone chlorides.

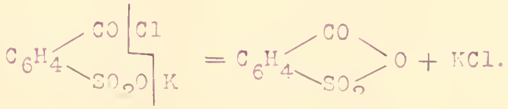
The formation of the anhydride, then, takes place in two stages, the first product being a monochlorinated derivative which passes into the anhydride by loss of potassium chloride.

I.



$$C_6H_4\begin{cases}COOK \\ SO_2OK\end{cases} + SOCl_2 = C_6H_4\begin{cases}COCl \\ SO_2OK\end{cases} + SO_2 + KCl.$$

II.



$$C_6H_4\begin{cases}CO\,|\,Cl \\ SO_2O\,|\,K\end{cases} = C_6H_4\begin{cases}CO \\ SO_2\end{cases}O + KCl.$$

The next experiment was performed with the intention of determining whether or not the anhydride could practically

prepared by this method. Thirty-four grams of the neutral potassium salt were treated with a large excess (7 or 8 mols.) of thionyl chloride and heated on the water-bath until no more sulphur dioxide escaped. About one hour was required. The excess of thionyl chloride was then distilled off and the residue in the flask was extracted with dry benzene. Only 7 grams (31%) of the anhydride was obtained, however. It seems probable that if the heating had been allowed to proceed longer, a larger yield would have been obtained; but the experiment was not repeated with the neutral salt, since the acid salt was found to give much more satisfactory results.

The final experiment with the neutral salt was an attempt to prepare a chloride of orthosulphobenzoic acid. Twenty grams of thionyl chloride was poured into a Carius tube and an equal weight of the neutral salt added, and a thorough mixture made. After heating at 125° for thirteen hours the tube was opened and found to contain anhydride, but no chloride was present. In order to isolate the chloride, if formed, the reaction mixture was shaken with water, ice and ether. Since the greater part of the anhydride was hydrolyzed by this process, the quantity formed was not determined.

EXPERIMENTS WITH THE ACID SALT. Both the neutral and acid potassium salts of orthosulphobenzoic acid are [illegible]

With the acid salt the reaction takes place with the formation of hydrochloric acid, showing that the point of attack is the carboxyl. With the acid salt, as with the neutral, no chloride was obtained either at ordinary pressure or in a sealed tube. As a method of preparing the anhydride, however, the action of thionyl chloride was found to be very satisfactory. Two experiments were conducted; in the first, 10 grams of the acid salt was heated on the water-bath with a large excess of thionyl chloride. The reaction was complete in forty-five minutes. After distilling off the excess of thionyl chloride, the residue was extracted with dry benzene. Four grams of the anhydride was obtained, which corresponds to a 52% yield.

The second experiment was conducted with somewhat larger quantities. Twenty-seven grams of the acid salt was heated on the water-bath with fifty-six grams of thionyl chloride. The volatile reaction products ceased to escape in about an hour, but the mixture was heated for one and one half hours longer, and was thus treated in the usual way. Sixteen and five tenths grams (80%) of the anhydride was obtained.

In order to get the best results, it has been found advisable to use a large excess of thionyl chloride. By so doing the mixture remains in a semi-liquid state, and better contact is secured. It is also advisable to [illegible]

[illegible] [illegible]. The thionyl chloride removed is quite pure and may be used again.

The results of these experiments indicate that the normal reaction of chlorinating agents on both the acid and neutral salts is the formation of a monochlorinated derivative containing the chlorine in combination with the carbonyl. This passes into the anhydride by the loss of potassium chloride. The formation of the two dichlorides of orthosulphobenzoic acid remains to be explained. In the preparation of the high-melting chlorides, about 60% of the low-melting chloride is also produced. When the neutral salt is treated in the same manner a mixture is also obtained. In this case the chlorinating agent is the pentachloride of phosphorus. On the other hand, in the preparation of the low-melting chloride by the action of phosphorus oxychloride on the neutral salt, practically none of the high melting chloride is formed. The formation of the high melting chloride, then , is favored by the action of a powerful chlorinating agent.

List and Stein(1)have shown that the action of phosphorus pentachloride on the anhydride at high temperatures gives rise to the formation of both chlorides. For the sake of comparison, the action of the oxychloride upon

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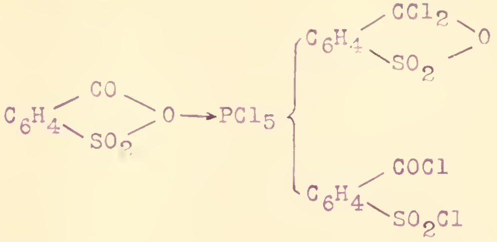
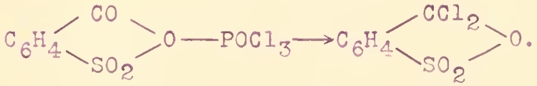
(1) Ber. d. chem. Ges. 31. 1659.

the anhydride, was tried. Twelve grams of the anhydride was heated for fourteen hours with phosphorus oxychloride at 125. At the end of that time the mixture was examined and it was found that, while the reaction was by no means complete, about two grams of the low-melting chloride had been formed. It was identified by its melting point. In order to test for the presence of high-melting chloride, ammonia was added but no sweet taste was produced. The action of phosphorus pentachloride probably takes place as follows: the anhydride is first formed and it is attacked in two ways by the pentachloride with the formation of two isomeric substances. The action of the oxychloride can take place in only one way, however, since only one product is formed. If the action of the oxychloride were not considered, one might assume that with the pentachloride, the reaction all goes in one direction, and that a rearrangement takes place. The fact that neither chloride can be changed into the other by heat, also argues against the latter supposition. The pentachloride, then, must have the power to chlorinate both the carboxyl group of the anhydride, and also to replace the anhydride oxygen atom. It would be expected that the latter reaction would take place with the greater difficulty, and as already stated, the yield of high-melting chloride when prepared from the acid salt is only 40 per cent of the total. The oxychloride is certainly [illegible] group. [illegible] though

chloride does not react with the anhydride:





VIII. EXPERIMENTS WITH MAGNESIUM PHENYL BROMIDE.

ACTION ON THE HIGH MELTING CHLORIDE.

With the high-melting chloride magnesium phenyl bromide reacts only upon boiling, while with the low-melting chloride the reaction is so violent that the solutions must be cooled with ice and mixed very slowly. The resulting products are very difficult to purify. In the case of the high-melting chloride the product has been fully identified, while with the low-melting chloride satisfactory results have not been obtained.

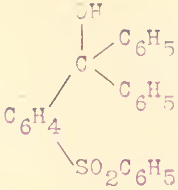
Ten grams of the high-melting chloride was dissolved in dry ether, and to the solution was added an ethereal solution of three and one half molecules of magnesium phenyl bromide. The mixture was boiled for an hour or two until the oily substance which settled to the bottom of the flask did not increase in quantity. At this point the ether above the oil had become clear. The ether was then

poured off and the residue in the flask was shaken with water and dilute hydrochloric acid. After the decomposition had been effected, the resulting oil was allowed to settle and the water and acid were poured off. It was washed with several changes of water. Steam was then conducted into the flask to remove any brombenzene which might have been present. After many unsuccessful attempts to purify this oil, the following method was found practicable. The oil was allowed to stand under water for a week or more. At the end of this time it had usually solidified for the most part. It was then heated to boiling with methyl alcohol, and the alcohol poured off while still hot. This treatment removed the unsolidified portion. The solid remaining was then crystallized from ethyl alcohol. The oil is easily soluble in alcohol and ether. After solidification, however, it is soluble in these solvents with much greater difficulty.

The product crystallized from alcohol melted at 183°- 184°. It is not affected by alcoholic potash. With concentrated nitric and sulphuric acids a dark red color is produced, an indication of the carbinol condition. Upon analysis the following figures were obtained:

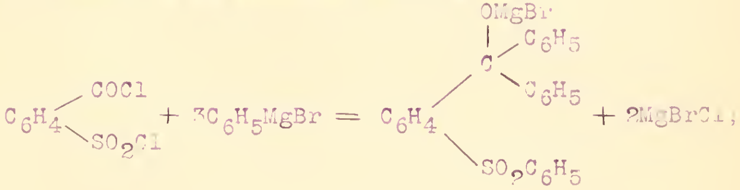
0.1284 gram gave 0.3509 gram CO_2 and 0.0603 gram H_2O.

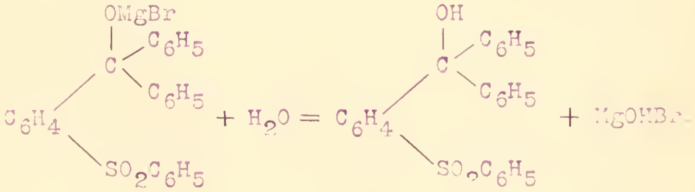
0. 2146 gram gave 0.1268 gram $BaSO_4$(Carius).

Calculated for  Found.

C	74.95%	74.52%
H	5.04	5.26
S	8.00	8.11

The reaction must be represented as follows:

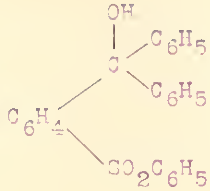
I. 

II. 

The structure of this substance was established by treating orthobenzoyldiphenylsulphone with magnesium phenyl bromide. The product thus obtained melted at the same temperature, and the melting point of the mixture remained unchanged. An analysis for carbon and hydrogen gave the following figures:

0.1378 gram gave 0.3783 gram CO_2 and 0.0661 gram H_2O.

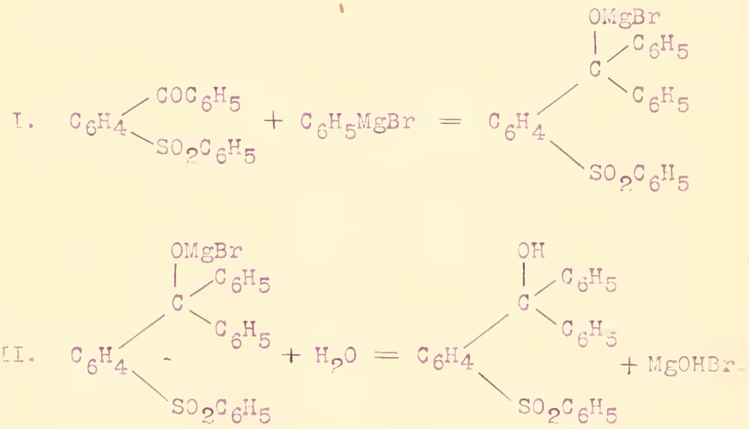
Calculated for



Found.

C	74.95%	74.86%
H	5.04	5.77

The reaction was:



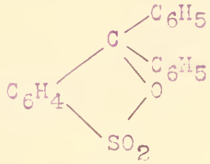
ACTION ON SULPHOBENZOIC ANHYDRIDE.

The reaction of magnesium phenyl bromide on sulpho-benzoic anhydride was tried in the hope of obtaining a di-phenylated derivative. This product was obtained and has been referred to under the reaction of benzene and aluminium chloride. The reaction is vigorous, and the solution should be cooled with ice. After standing over night, water and hydrochloric acid were A [illegible] and the [illegible]

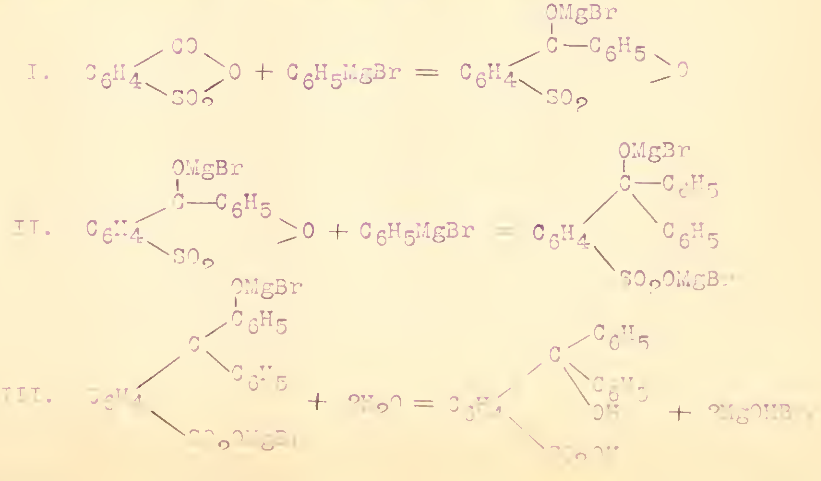
[illegible] shaken with ether. Upon evaporation of the ethereal layer a product was obtained which, upon crystallized from alcohol, melted sharply at 167° (uncorr.). It dissolved in alcoholic potash, on boiling, with the formation of a salt soluble in water. Upon acidification the original substance was precipitated. Neither water nor aqueous potash would dissolve the substance even when boiled. Analysis gave the following figures:

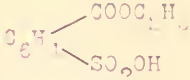
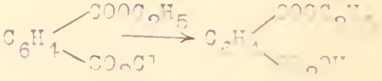
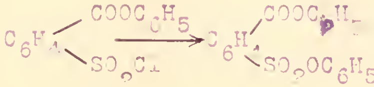
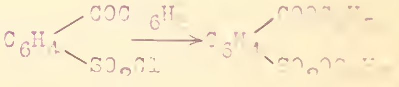
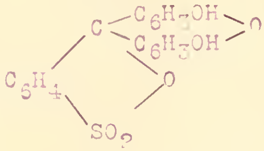
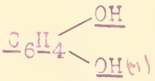
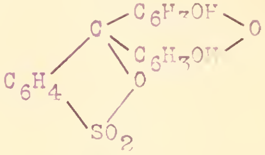
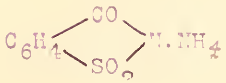
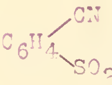
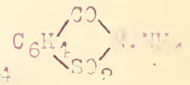
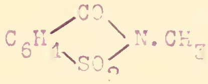
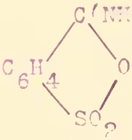
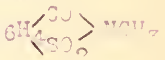
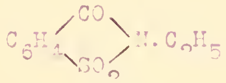
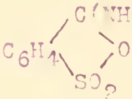
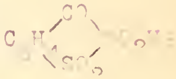
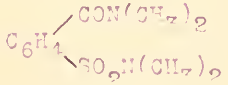
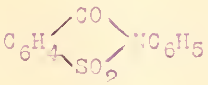
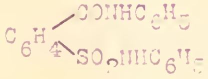
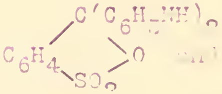
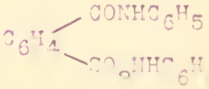
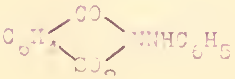
I. 0.1070 gram gave 0.2772 gram CO_2 and 0.0447 gram H_2O.

II. 0.2056 gram gave 0.1561 gram $BASO_4$ (Carius).

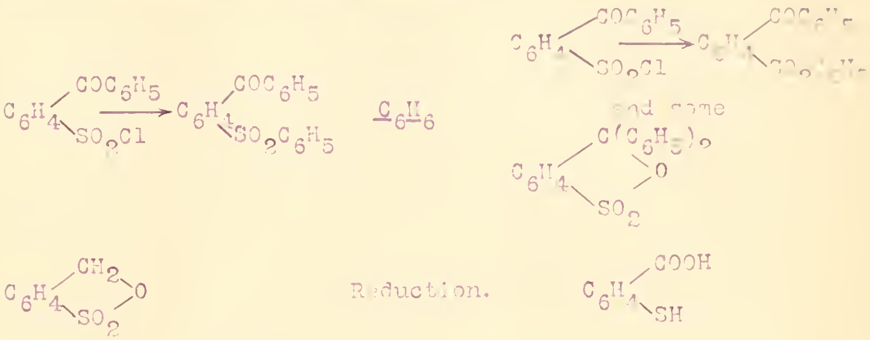
	Calculated for 	Found.
C	70.76%	70.64%
H	4.38	4.68
S	9.95	10.40

The reaction may be expressed as follows:



High-boiling Chloride.	Reagent.	Low-melting Chloride.
	C_2H_5OH	
	C_6H_5OH	
		
	NH_3	 and some 
	CH_3NH_2	 and some 
	$C_2H_5NH_2$	 and some 
	$(CH_3)_2NH$	Not definitely characterized.
 and 	$C_6H_5NH_2$	 and some 
	$C_6H_5NHNH_2$	Not definitely characterized.

High-melting Chloride. Reagent. Low-melting Chloride.



X. CONCLUSIONS.

From this table it will be seen that with water, the alcohols and alcoholates both chlorides give the same products and that they are symmetrical. Benzene and aluminium chloride have undoubtedly yielded an unsymmetrical derivative in at least two instances, but the tendency is to form the same symmetrical product with both chlorides.

In contrast to these reactions are those of ammonia and the amines. With the high-melting chloride, the products always indicate its symmetrical nature. With the low-melting chloride, however, the products may vary with the conditions, or both the symmetrical and unsymmetrical products may be found in the same reaction. These facts indicate that the products pass from the unsymmetrical to the symmetrical and not in the opposite direction.* The

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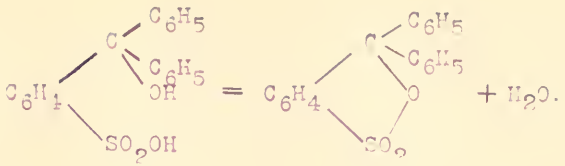
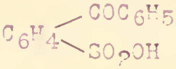
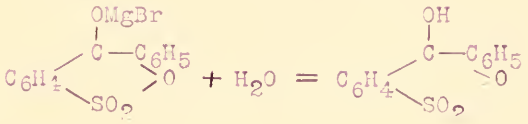
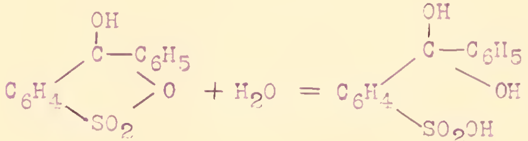
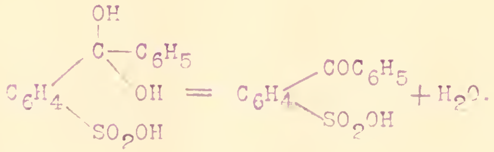
*[illegible] this [illegible] is known. When either chloride is heated with [illegible], [illegible] an unsymmetrical [illegible] is obtained.

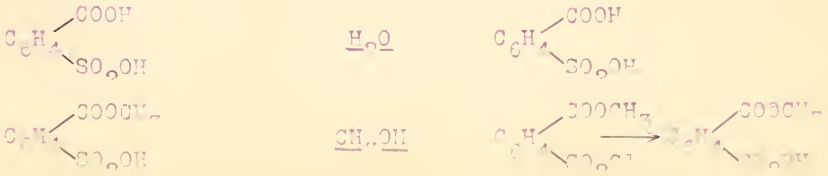
IV. 

The substance just described is formed to the extent of only about ten per cent. It is probable that the reaction, in the main, stops at stage I. The product would then be hydrolyzed to form the acid  $C_6H_4\langle{}^{COC_6H_5}_{SO_2OH}$ as follows:

I. 

II. 

III. 



conclusion must be, then, that the stable form of the derivatives is the symmetrical. The unsymmetrical form may be unstable to such a degree that it cannot exist as in the case of the esters, and alcoholic derivatives in general. With the nitrogen derivatives there is a greater degree of stability, and the unsymmetrical forms are found to exist. The tendency to pass into the stable form, however, is shown here by the fact that both isomers are found in the same reaction.

It should be borne in mind that no conclusion can be drawn concerning the structure of the chlorides from any one reaction. From the results of the many investigations here tabulated the only rational conclusion seems to be that the chlorides are distinct chemical individuals, the one melting at 79°.5 being symmetrical, the one melting at 40° being unsymmetrical.

XI. THE CHLORIDES OF DIBASIC ACIDS IN GENERAL.

In order to show the analogies which exist between the chlorides of orthosulphobenzoic acid and those of certain other dibasic acids, a brief account of the conduct of the latter has been prepared.

The chlorides of dibasic acids of the aliphatic series which have been most extensively studied are those of succinic, maleic, and glutaric acids, while in the aromatic series, phthalyl chloride and the chlorides of orthosulphobenzoic, [illegible]

ignited.

Phthalyl chloride was first prepared by Müller(1) by allowing phosphorus pentachloride to act upon phthalic acid, or its anhydride. He treated the chloride thus obtained with water, and regenerated the original acid. Kolbe and Wischin(2) reduced the chloride by means of zinc and aqueous hydrochloric acid, and obtained, as they supposed, an aldehyde of the formula $C_6H_4{<}\genfrac{}{}{0pt}{}{CHO}{CHO}$. This was shown later by Hessert(3) to correspond rather to the reactions of a lactone than of an aldehyde, and accordingly he assigned to it the formula of phthalide: $C_6H_4{<}\genfrac{}{}{0pt}{}{CH2}{CO}{>}O$. A short time after this Friedel and Craft allowed benzene to react upon phthalyl chloride in the presence of aluminic chloride, and obtained a diphenylated derivative which they supposed was to be represented by the formula $C_6H_4{<}\genfrac{}{}{0pt}{}{COC_6H_5}{COC_6H_5}$. Baeyer(5) who was engaged at this time upon the study of the phthaleins, having had occasion to prepare this substance found that when boiled with alcoholic potash it dissolved with the formation of the potassium salt of an oxyacid. Upon treatment with acids the original substance was precipitated. While these changes pointed clearly to the

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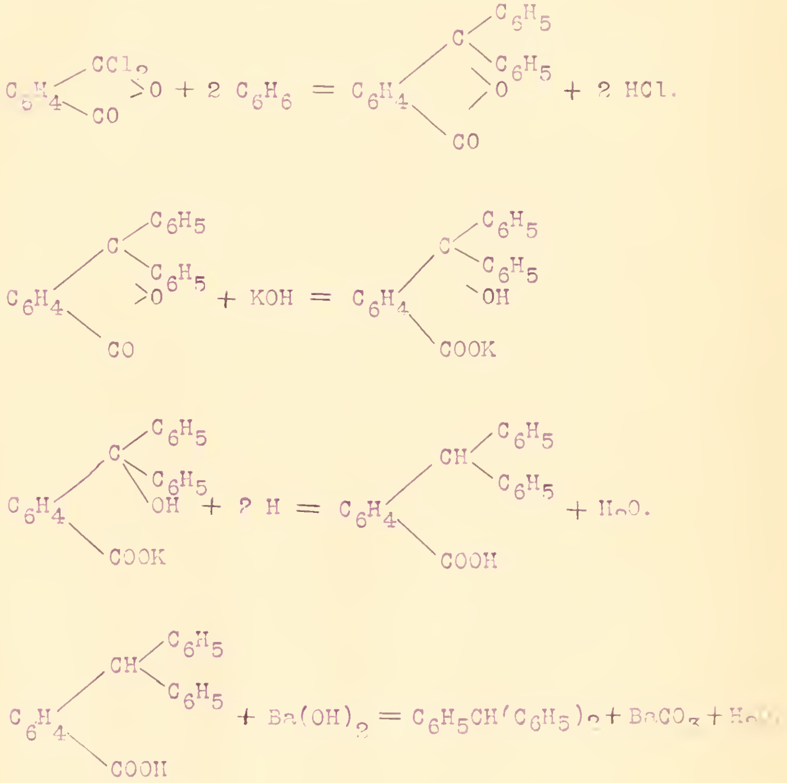
(1) Zeit. Chem. Pharm. 1863. 257.
(2) Z. Chem. (2) II. 315.
(3) Ber. d. chem. Ges. 10. 1445.
(4) Compt. rend. Jan 11. 1877.
(5) Ann. Chem. 202. 50.

second formula for the compound, Baeyer sought still further evidence. He accordingly reduced the above potassium salt by means of zinc in alkaline solution, and obtained a carboxyl acid, which when distilled with barium hydroxide gave him triphenylmethane. The reaction involved must be expressed as follows:



Friedel(1) taking into consideration the formation of phthalide proposed to ascribe the unsymmetrical

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(1) Bull. Soc. Chim. 32. 595.

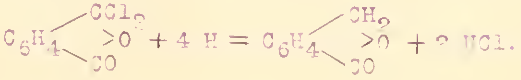
formula to phthalyl chloride, thus removing the difficulty in the interpretation of the above reaction.

Since the reactions in the presence of aluminic chloride are often attended by molecular rearrangements it was thought possible that the formation of the unsymmetrical diphenyl derivative might be due to this cause. This objection was removed, however, by Nölting and Bechi[1] who obtained the same product by the action of mercury diphenyl.

These facts point unmistakeably to the unsymmetrical formula for phthalyl chloride. There are, on the other hand, certain facts which seem to point toward the symmetrical formula for this substance.

In his article upon the chlorides of dibasic acids Auger[2] discusses these objections and gives an account of his own experiments on this and other analogous substances.

1. The formation of the orthophthalyl alcohol by reduction with sodium amalgam in acetic acid, a reaction seeming to point to the symmetrical formula, he thinks may indeed be the normal reaction of an unsymmetrical structure, thus:



$$C_6H_4\begin{matrix} \diagup CCl_2 \\ >O \\ \diagdown CO \end{matrix} + 4\,H = C_6H_4\begin{matrix} \diagup CH_2 \\ >O \\ \diagdown CO \end{matrix} + 2\,HCl.$$

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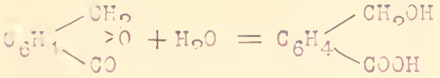
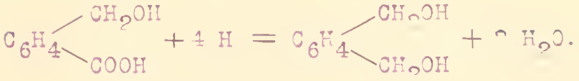
[1] Ber. d. chem. Ges. 17. 385.
[2] Ann. Chim. Phys. (6) 22. 289.

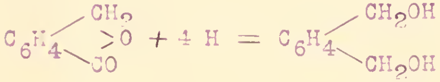


$$C_6H_4\left\langle\begin{matrix}CH_2\\CO\end{matrix}\right\rangle O + H_2O = C_6H_4\left\langle\begin{matrix}CH_2OH\\COOH\end{matrix}\right.$$



$$C_6H_4\left\langle\begin{matrix}CH_2OH\\COOH\end{matrix}\right. + 4\ H = C_6H_4\left\langle\begin{matrix}CH_2OH\\CH_2OH\end{matrix}\right. + 2\ H_2O.$$

or more simply:



$$C_6H_4\left\langle\begin{matrix}CH_2\\CO\end{matrix}\right\rangle O + 4\ H = C_6H_4\left\langle\begin{matrix}CH_2OH\\CH_2OH\end{matrix}\right.$$

2. The question of the identity of the esters of phthalic acid whether prepared from the silver salt and an alkyl iodide, or by means of the chloride and an alcoholate, has been settled by Graebe(1), who found them to be identical whether prepared by one method or the other. In the case of the esters of tetrachlor phthalic acid, however, Graebe found isomerism.

The action of ammonia upon phthalyl chloride has been the subject of several investigations. Kuhara(2) mixed the chloride with ammonia, and after the reaction had taken place added hydrochloric acid in excess. He then heated the mixture in order to dissolve the precipitate which had been formed upon the addition of the acid. Upon cooling, ordinary phthalimide crystallized out. He also obtained on one occasion a substance isomeric with phthalimide melting at 192°. These experiments could best be interpreted by assuming the symmetrical

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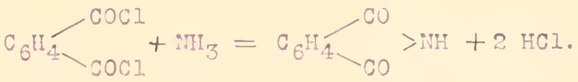
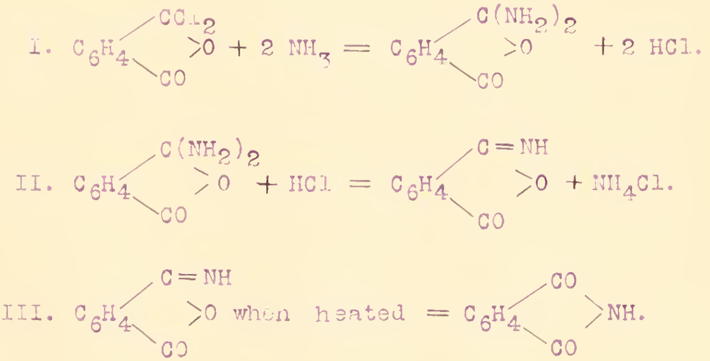
(1) Ber. d. chem. Ges. 16. 860.
(2) Am. Chem. J. 3. 2[illegible]

formula for phthalyl chloride:



$$C_6H_4\begin{matrix}\diagup COCl\\ \diagdown COCl\end{matrix} + NH_3 = C_6H_4\begin{matrix}\diagup CO\\ \diagdown CO\end{matrix}\!>NH + 2\,HCl.$$

In repeating the work of Kuhara, Auger[1] obtained quite different results. He isolated a substance which he considered to be the unsymmetrical diamide and from it by the action of hydrochloric acid he passed to what he supposed to be the corresponding imide. This imide melted at 145° to a clear liquid which soon solidified and subsequently melted at 228°, the melting point of the symmetrical imide. He represented the reactions as follows:



$$\mathrm{I.}\quad C_6H_4\begin{matrix}\diagup CCl_2\\ \diagdown CO\end{matrix}\!>O + 2\,NH_3 = C_6H_4\begin{matrix}\diagup C(NH_2)_2\\ \diagdown CO\end{matrix}\!>O + 2\,HCl.$$

$$\mathrm{II.}\quad C_6H_4\begin{matrix}\diagup C(NH_2)_2\\ \diagdown CO\end{matrix}\!>O + HCl = C_6H_4\begin{matrix}\diagup C{=}NH\\ \diagdown CO\end{matrix}\!>O + NH_4Cl.$$

$$\mathrm{III.}\quad C_6H_4\begin{matrix}\diagup C{=}NH\\ \diagdown CO\end{matrix}\!>O \text{ when heated } = C_6H_4\begin{matrix}\diagup CO\\ \diagdown CO\end{matrix}\!>NH.$$

Had these reactions remained unquestioned they would have been regarded as strong evidence for the unsymmetrical formula of the chloride. In a later investigation Hoogewerff and Van Dorp[2] showed that Auger was deal-

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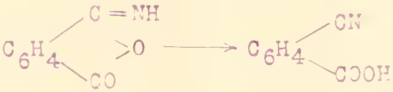
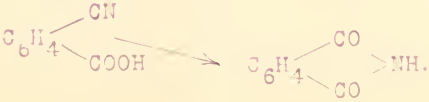
[1] Loc. cit.
[2] Rec. Trav. Chim. 11, 84.

ing with an impure substance, and that the product formed by the action of ammonia on the chloride is in reality orthocyanobenzoic acid. It was this substance in the impure state which Auger had described as the unsymmetrical imide. The pure cyan acid melts between 180° and 190°, depending upon the rapidity of the heating, and is transformed into the symmetrical imide. This transformation is also effected by boiling with water. Kuhara had obtained the cyan acid once in a pure condition, but his failure to obtain it a second time lay in the method of purification which he adopted. As has been said, boiling with water converts the acid into the symmetrical imide, and it was this substance which Kuhara obtained from the reaction. Hoogewerff and Van Dorp believe that the conversion of the chloride into the cyan acid takes place as follows. The first action of the ammonia causes the formation of an unsymmetrical imide, which is unstable in the alkaline solution and immediately passes into the cyan acid by a molecular re-arrangement:



$$C_6H_4\begin{cases}C{=}NH \\ \quad >O \\ CO\end{cases} \longrightarrow C_6H_4\begin{cases}CN \\ COOH\end{cases}$$

The transformation of the cyan acid into the symmetrical imide is also accompanied by a molecular re-arrangement:

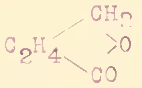


$$C_6H_4\begin{cases}CN \\ COOH\end{cases} \longrightarrow C_6H_4\begin{cases}CO \\ \quad >NH. \\ CO\end{cases}$$

The weight of evidence seems to argue so strongly for the unsymmetrical nature of phthalyl chloride that little if any doubt of its correctness can exist.

SUCCINYL CHLORIDE.

Succinyl chloride was discovered by Gerhardt and Chiozza.(1) The reduction of the chloride was first studied by Saytzeff,(2) who regarded the product thus obtained as succinic aldehyde, in consideration of certain of its reactions; and it was not until 1880 that Bredt(3) pointed out that its chemical conduct placed it in the class of lactones. He accordingly assigned to it the formula:



$$C_2H_4\begin{cases}CH_2\\ \quad >O\\ CO\end{cases}$$

analogous to phthalide. In the same year this conclusion was reached by Saytzeff by a different method.

In studying the action of benzene, in the presence of aluminic chloride, upon succinyl chloride, Auger observed that while 90 per cent of the reaction product was, as in the case of phthalyl chloride, a lactone, a small quantity, about 10 per cent of the isomeric symmetrical product was always obtained. The former must then be derived from a chloride of the unsymmetrical variety, while the latter

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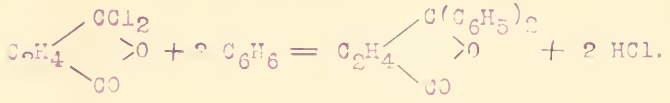
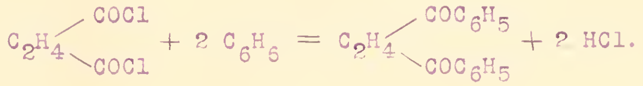
(1) Ann. Chem. 87. 293.
(2)
(3) Ber. d. chem. Ges. 13. 748.

is derived from the symmetrical chloride thus :





In the reactions with ammonia Auger describes the formation of an unsymmetrical diamide and imide as in the case of phthalyl chloride. It is probable that his observations were in error,(1) however, and that the reaction proceeds as has been pointed out in the latter case by Hoogewerff and Van Dorp.

The chloride of malonic acid was prepared by Auger by allowing thionyl chloride to react upon the free acid. The chloride was submitted to investigation with the purpose of determining whether it too was of the unsymmetrical structure. The reaction of benzene and aluminic chloride gave as the final product dibenzoyl methane, a symmetrical compound. Among the reactions already known, the condensation of malonic and urea in the presence of the oxychloride of phosphorus to form barbituric acid, pointed to the symmetrical formula for the chloride of malonic acid. With the chloride of ethyl malonic acid the reactions with all reagents were found to be analogous.

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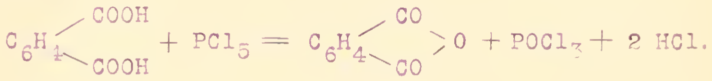
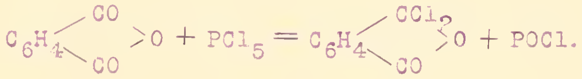
(1) Vorländer, Ber. d. chem. Ges. 30. 2268 (Note).

In the cases just considered, it is seen that those acids from which unsymmetrical chlorides have been obtained are those having their carboxyl groups in the γ or 1 - 4 positions. Since these acids form anhydrides, the formation of unsymmetrical chlorides may be explained by assuming the intermediate formation of the anhydride and the subsequent action upon it by the chlorinating agent used:



$$C_6H_4\left<\begin{matrix}COOH\\COOH\end{matrix}\right. + PCl_5 = C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O + POCl_3 + 2\ HCl.$$

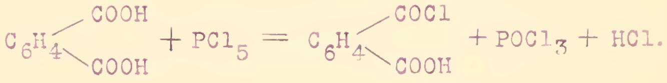


$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O + PCl_5 = C_6H_4\left<\begin{matrix}CCl_2\\CO\end{matrix}\right>O + POCl.$$

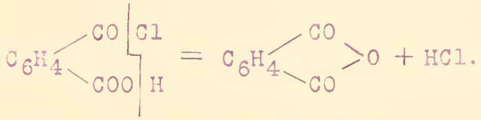
On the other hand there is the possibility that the intermediate formation of an anhydride does not govern the formation of the unsymmetrical chloride, but that the γ position of the carboxyls is the determining influence. In order to test this point Auger resorted to glutaric acid. Here the carboxyl groups are in the 1 - 5 or δ position. The acid forms an anhydride on simple distillation, however. The pentachloride of phosphorus would in all probability bring about this change, and the resulting chloride would be unsymmetrical if its formation is conditioned by the presence of anhydride. An examination of the chloride of glutaric acid showed it to be symmetrical, however, no trace of an isomeric substance

being found. Auger therefore concludes that the formation of unsymmetrical chlorides from the 1 - 4 carboxylic acids is due to the influence of this position of the carboxyls and is not dependent upon the intermediate formation of the anhydride.

Another explanation of the facts above referred to seems possible to the present writer. The formation of anhydride by the action of phosphorus pentachloride on organic acids probably takes place in two steps as follows:

I. 

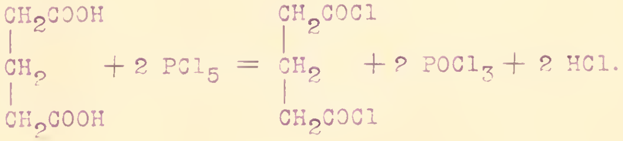
$$C_6H_4\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix} + PCl_5 = C_6H_4\begin{matrix}\diagup COCl\\ \diagdown COOH\end{matrix} + POCl_3 + HCl.$$

II. 

$$C_6H_4\begin{matrix}\diagup CO\,|\,Cl\\ \diagdown COO\,|\,H\end{matrix} = C_6H_4\begin{matrix}\diagup CO\\ \diagdown CO\end{matrix}\!>O + HCl.$$

The chlorination of only one of the carboxyl groups being due to the fact that they are in the ortho position. With succinic acid the same tendency would be present. The tendency to form anhydrides becomes less as the distance between the carboxyl groups is increased, glutaric acid being the last member of a series to yield an anhydride on simple distillation. In the aromatic series meta and para anhydrides are not formed. With the decreasing tendency to form anhydrides the tendency to form unsymmetrical chlorides disappears, a fact which can be explained by assuming that the removal of the interfering [illegible]

of the carboxyls leaves both of them susceptible to the simultaneous attack of the chlorinating agent. This would result in the formation of a symmetrical chloride as follows:



$$\begin{matrix} CH_2COOH \\ | \\ CH_2 \\ | \\ CH_2COOH \end{matrix} + 2\ PCl_5 = \begin{matrix} CH_2COCl \\ | \\ CH_2 \\ | \\ CH_2COCl \end{matrix} + 2\ POCl_3 + 2\ HCl.$$

The formation of unsymmetrical chlorides from 1-4 acids may then be dependent upon the intermediate formation of the anhydride.

BIOGRAPHICAL.

Philip Howard Cobb was born in Portland, Maine, November 15, 1880. His early education was received in the public schools of that city. In the fall of 1898 he entered Bowdoin College, and was graduated in June 1902 with the degree of Bachelor of Arts. Since that time he has been engaged in the study of Chemistry at the Johns Hopkins University. His subordinate subjects have been Physical Chemistry and Mineralogy. In 1903-1904 he was Assistant to Dr. Gilpin, and is at present Lecture Assistant to Dr. Renouf.